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(54) PROTON CONDUCTIVE MEMBRANE FOR DIRECT TYPE ALCOHOL FUEL CELL AND DIRECT TYPE ALCOHOL FUEL CELL UTILIZING THE SAME

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a proton conductive membrane for direct type alcohol fuel cell having a high proton conductivity and excellent blocking property to alcohol.
SOLUTION: This proton conductive membrane for direct type alcohol fuel cell mainly comprises a polyimide partly including a proton conductive substituent.

LEGAL STATUS

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the proton conductivity film for direct alcoholic mold fuel cells which uses alcohols, such as a methanol, as a direct fuel, and the direct alcoholic mold fuel cell which used it in the polymer electrolyte fuel cell which uses the proton conductivity film as an electrolyte.
[0002]
[Description of the Prior Art] A polymer electrolyte fuel cell is a cell which equips with two electrodes the both sides of the electrolyte which consists of a poly membrane which has proton conductivity, supplies oxidation gas (oxidizer), such as oxygen and air, to one electrode, supplies fuels (reducing agent), such as hydrogen and a hydrocarbon, to the electrode of another side, is made to cause electrochemical reaction, and is made to generate the electrical and electric equipment.
[0003] There are some classes of fuel cells according to the class of the electrolyte to be used or fuel, and what uses especially a methanol for a direct fuel is called direct methanol mold fuel cell (it abbreviates to DMFC hereafter). as compared with using the hydrogen in which many fuel cells reformed hydrogen or a hydrocarbon, in order to supply a methanol to a direct anode electrode, a fuel tends to deal with DMFC, and equipment is simple -- becoming -- home use and industrial use -- it is comparatively expected as a power source of the Koide force scale. The direct methanol mold fuel cell is seen as a hopeful as a future power source of a noncommercial pocket device like especially a cellular phone and a notebook sized personal computer.
[0004] The theoretical output voltage of a methanol-oxygen fuel cell is the 1.2V [almost same] (25 degrees C) as what uses hydrogen as a fuel, and can expect a property equivalent to a hydrogen-oxygen fuel cell theoretically. Much researches are made and the engine performance has [a remarkable improvement] ****** inadequate [the engine performance] about DMFC which used the solid-state polyelectrolyte, as compared with the engine performance of a hydrogen-oxygen fuel cell as compared with an early thing. It is the cause that this has the high methanol permeability of an electrolyte membrane besides the ability to have not found out catalyst with the sufficient oxidation activity of a methanol.
[0005] As a former and solid-state polyelectrolyte, it is Du. The perfluoro sulfonic-acid film represented by Nafion (trademark) of Pont has mainly been examined. Generally these film is supposed that methanol cutoff nature is low, the crossover of a methanol arises and a desired cell property is not discovered when it is used as film for DMFC (J. T.Wang, J.S.Wainright, R.F.Savinelland M.Litt J.Appl.Electrochem., 26,751(1996).). Sufficient property is not acquired, although the approach of supplying a methanol by the gaseous phase and lowering the methanol concentration by the side of a membranous anode etc. is reported while setting reaction temperature as 100 degrees C or more and

gathering the oxidation rate of a methanol in order that DMFC using these film may solve the above-mentioned problem. moreover, as an approach of improving the methanol permeability of other polyelectrolyte film How to use the film which carried out heat bridge formation of the high molecular compound which contains polystyrene sulfonate and polyvinyl alcohol on a porosity base material (JP,5-174856,A), the approach (JP,11-3724,A --) of preparing the layer which carries out the trap of the methanol into an electrolyte membrane, and discharging outside Although the approach (JP,11-135137,A, JP,11-144745,A, JP,11-273695,A) of using JP,11-26005,A and the anion exchange film etc. is examined Sufficient property has not been acquired in respect of a cell property, the long-term stability of an electrolyte membrane, etc.

[0006]

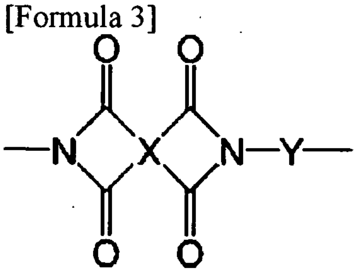
[Problem(s) to be Solved by the Invention] The purpose of this invention has the low permeability of alcohols, such as a methanol usable as an electrolyte membrane of direct alcoholic mold fuel cells including a direct methanol mold fuel cell, and is to offer the proton conductivity film for direct alcoholic mold fuel cells which has high proton conductivity and the direct alcoholic mold fuel cell which used it, and a direct methanol mold fuel cell.

[0007]

[Means for Solving the Problem] That is, this invention is proton conductivity film for direct alcoholic mold fuel cells which makes a main constituent polyimide including the repeat unit expressed with the following general formula (I).

[0008]

[Formula 3]



(I)

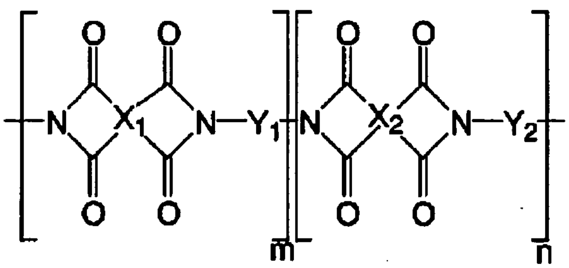
[-- X shows at least one sort of tetravalent organic radicals among a formula, Y shows at least one sort of divalent organic radicals, and a part of X and Y contain a proton conductivity substituent.]

At least one sort chosen from the group which consists of a phenolic hydroxyl group, a sulfonic group, a carboxylic-acid radical, and a phosphoric-acid radical can be used for said proton conductivity substituent.

[0009] Moreover, as for said polyimide, it is desirable that it is polyimide including the repeat unit expressed with the following general formula (II).

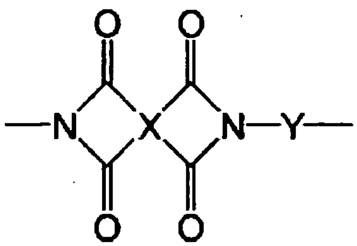
[0010]

[Formula 4]



(I I)

A different tetravalent organic radical, the divalent organic radical on which Y1 contains a proton conductivity substituent, and Y<SUB>2 are that X1 and X2 are the same or a thing which shows the divalent organic radical which does not contain a proton conductivity substituent among [type. m is one or more integers and n is zero or more integers.]
In this invention, it is desirable that the repeat unit of m of polyimide includes the repeat structural unit acquired according to the polyfunctional component in which it is desirable that the repeat unit of n is 15-80-mol %, and polyimide contains three or more amino groups 20-85-mol%, and the polycondensation of tetracarboxylic dianhydride.
[0011] As for the repeat structural unit acquired according to the polyfunctional component containing three or more amino groups, and the polycondensation of tetracarboxylic dianhydride, it is desirable that it is the 0.1-20-mol range of %, and, as for polyimide, it is still more desirable that it is polyimide obtained according to the polycondensation of the diamine containing tetracarboxylic dianhydride and a proton conductivity substituent and/or the diamine which does not contain a proton conductivity substituent.
[0012] as the diamine which it is desirable that it is 1, 4, 5, and 8-naphthalene tetracarboxylic dianhydride as for tetracarboxylic dianhydride, and contains a proton conductivity substituent -- 2 and 2 - benzidine sulfonic acid, 2, 4-diaminobenzene sulfonic acid, 2, 5-diaminobenzene sulfonic acid, and '3, 3' -- the - dimethyl -4 and 4' - diamino biphenyl -6 and 6' -- it is desirable that it is at least one sort chosen from the group which consists of a - disulfon acid. As for the diamine which does not contain a proton conductivity substituent on the other hand, it is desirable that it is at least one sort chosen from the group which consists of a - diamino diphenyl ether, p phenylenediamine, and 9 and 9-bis(4-aminophenyl) fluorene, 4, and 4 '2, 2' bis[-] [4-(4-amino phenoxy) phenyl] propane.
[0013] The fuel cell of this invention is a direct alcoholic mold fuel cell which used the above-mentioned proton conductivity film, and it is desirable that operating temperature is 50 degrees C or less.
[0014]
[Embodiment of the Invention] The direct alcoholic mold fuel cell and direct methanol mold fuel cell which used the proton conductivity film for direct alcoholic mold fuel cells and it concerning this invention for below are explained concretely.
[0015] As for the proton conductivity film of this invention, it is desirable to make the polyimide of the configuration of either the following type (I) or (II) into a main constituent.
[0016]
[Formula 5]

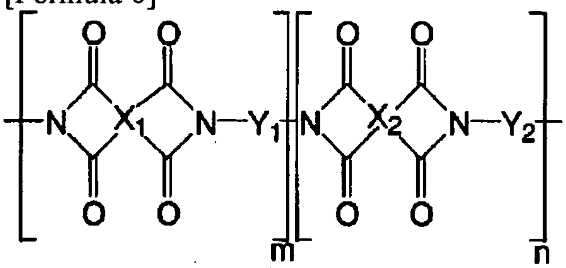


(I)

[-- X shows at least one sort of tetravalent organic radicals among a formula, Y shows at least one sort of divalent organic radicals, and a part of X and Y contain a proton conductivity substituent.] Polyimide which comes out and includes the repeat unit expressed.

[0017]

[Formula 6]



(I I)

A different tetravalent organic radical, the divalent organic radical on which Y1 contains a proton conductivity substituent, and Y2 are that X1 and X2 are the same or a thing which shows the divalent organic radical which does not contain a proton conductivity substituent among [type. m is one or more integers and n is zero or more integers.] Polyimide which comes out and includes the repeat unit expressed.

[0018] With the substituent which has the proton conductivity of this invention, a phenolic hydroxyl group, a sulfonic group, a carboxylic-acid radical, a phosphoric-acid radical, etc. are mentioned. The sulfonic group and phosphoric-acid radical which a proton tends to dissociate from the point of making high proton conductivity discovering especially are desirable. When using the polyimide containing an aromatic series ring etc. as the introductory approach of proton conductivity substituents, such as a sulfonic group, it can carry out by the approach of well-known sulfonation of an aromatic series system compound. After preparing the polyimide which prepared the organic solvent solution and suspension of polyimide, added the sulfonation agent, was mixed as such an approach, and introduced the sulfonic group, the approach of forming membranes and obtaining the proton conductivity film, the method of making the polyimide film immersed in an organic solvent, adding a sulfonation agent, and obtaining the proton conductivity film, etc. are mentioned. The aromatic series organic sulfonic acid represented with this invention by the mixed liquor of the mixed liquor of a sulfuric acid, a sulfuric acid, and an aliphatic series acid anhydride, a chlorosulfonic acid, a chlorosulfonic acid, and chlorination trimethylsilyl, a sulfur trioxide, a sulfur trioxide, and triethyl phosphate, further 2, 4, and 6-trimethyl benzenesulfonic acid as an usable sulfonation agent can be illustrated. Moreover, as an organic solvent to be used, ring type aliphatic hydrocarbon, such as straight chain type aliphatic hydrocarbon, such as halogenated hydrocarbon, such as a methylene chloride, and a hexane, and a

cyclohexane, can be illustrated. These sulfonation agents and organic solvents may be suitably chosen from two or more combination if needed.

[0019] Moreover, the method of using the monomer component containing a proton conductivity substituent, compounding polyimide, forming membranes, and obtaining the proton conductivity film is more simple, and desirable. That simplification of manufacture and a proton conductivity substituent are trustworthy, and by distributing to homogeneity, it is easy to discover a property and especially the thing for which the polyimide obtained according to the polycondensation of the diamine containing tetracarboxylic dianhydride and a proton conductivity substituent and/or the diamine which does not contain a proton conductivity substituent is used is desirable.

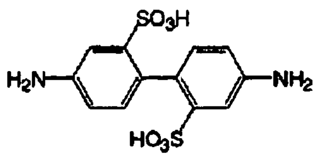
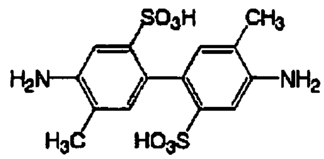
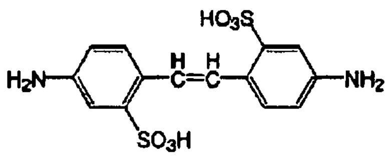
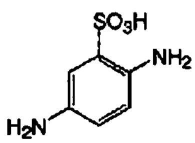
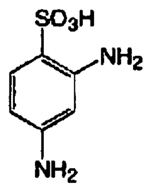
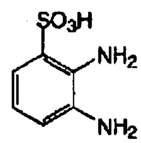
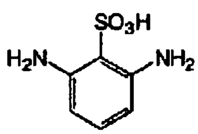
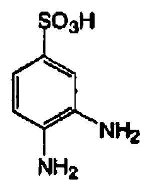
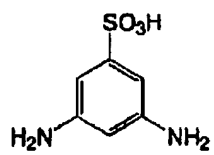
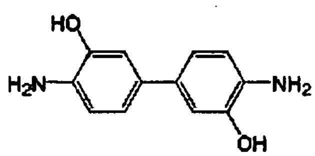
[0020] As for the proton conductivity film of this invention, it is desirable to include the repeat structural unit acquired by the polycondensation reaction of the polyfunctional component containing three or more amino groups and tetracarboxylic dianhydride. By containing such a constituent, proton conductivity improves remarkably.

[0021] As tetracarboxylic dianhydride used for this invention For example, Para-terphenyl - 3, 4, 3'', 4''-tetracarboxylic dianhydride, Pyromellitic acid 2 anhydride, 3, 3', 4, 4'-benzophenone tetracarboxylic dianhydride, 3, 3', 4, 4'-biphenyl ether tetracarboxylic dianhydride, 1, 2, 5, 6-naphthalene tetracarboxylic dianhydride, 2, 3 and 6, 7-naphthalene tetracarboxylic dianhydride, 2, 3, 5, 6-pyridine tetracarboxylic dianhydride, 1, 4 and 5, 8-naphthalene tetracarboxylic dianhydride, 3, 4, 9, 10-perylene tetracarboxylic dianhydride, 4, and 4'-sulfonyl diphthalic acid dianhydride, 3,3',4,4'-tetraphenylsilane carboxylate dianhydride, Meta-terphenyl -3, 3'', 4, 4''-tetracarboxylic dianhydride, 3, 3', 4, 4'-diphenyl ether tetracarboxylic dianhydride, 1, 3-screw (3, 4-dicarboxy phenyl) - 1, 1, 3, and 3-tetramethyl disiloxane 2 anhydride, 1-(2, 3-dicarboxy phenyl)-3-(3, 4-dicarboxy phenyl)-1, 1 and 3, and 3-tetramethyl disiloxane 2 anhydride, 2 and 2-bis(3, 4-dicarboxy phenyl) hexafluoropropane acid 2 anhydride, one -- two -- three -- four - butane -- tetracarboxylic dianhydride -- one -- three -- three -- a -- four -- five -- nine -- b - hexahydro - five - (tetrahydro - 2, 5-dioxo 3-furanyl) - naphth one -- [-- one -- two - c --] -- a furan - one -- three - dione -- etc. -- mentioning -- having -- although -- this -- limiting -- having -- a thing -- it is not . When the chemical stability, especially deck-watertight-luminaire (acid) nature at the time of using it as proton conductivity film for direct alcoholic mold fuel cells are especially taken into consideration in this invention, it is desirable that it is 1, 4, 5, and 8-naphthalene tetracarboxylic dianhydride.

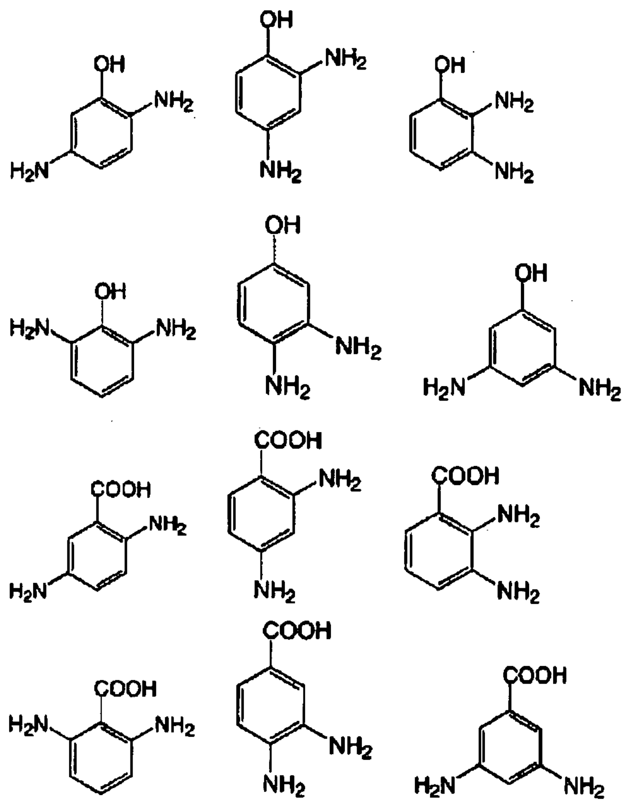
[0022] As diamine containing the substituent which has proton conductivity, although the following compound etc. is mentioned, for example, it is not limited to this.

[0023]

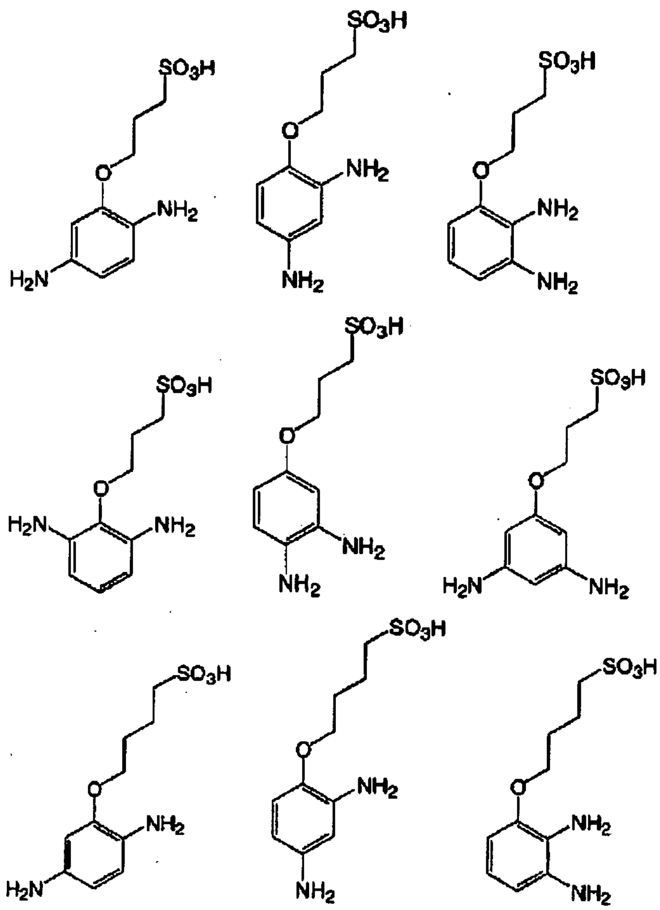
[Formula 7]

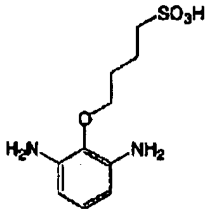
[0024]
[Formula 8]

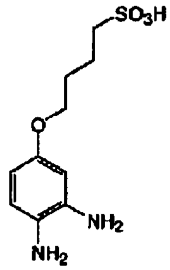


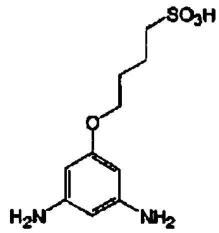
[0025]
[Formula 9]

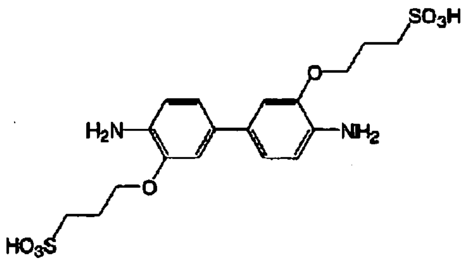


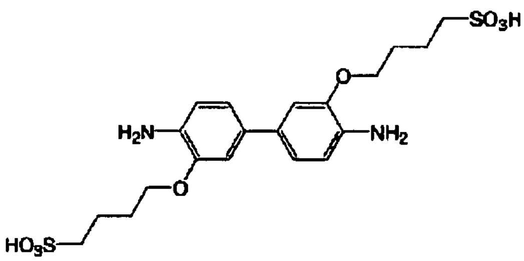
[0026]
[Formula 10]







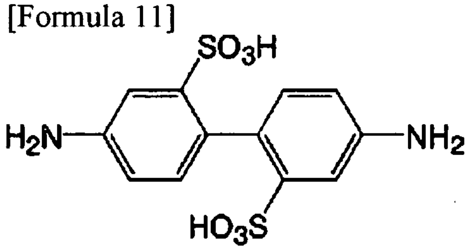




Especially in this invention, if proton conductivity etc. is taken into consideration in the stability of a compound, the ease of industrial acquisition, and the ease of carrying out of composition of polyimide 2 expressed with following chemical formula (III)- (VI), a 2'-benzidine sulfonic acid (III), 2, 4-diaminobenzene sulfonic acid (IV), 2, 5-diaminobenzene sulfonic acid (V), 3, and 3' -- the - dimethyl -4 and 4' - diamino biphenyl -6 and 6' -- it is desirable that it is at least one sort chosen from - disulfon acid (VI).

[0027]

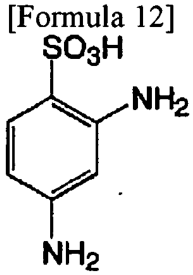
[Formula 11]



(III)

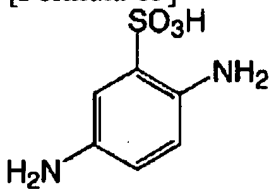
[0028]

[Formula 12]



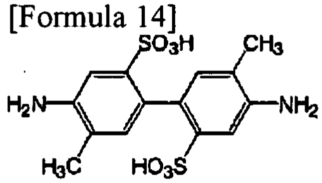
(IV)

[0029]
[Formula 13]



(V)

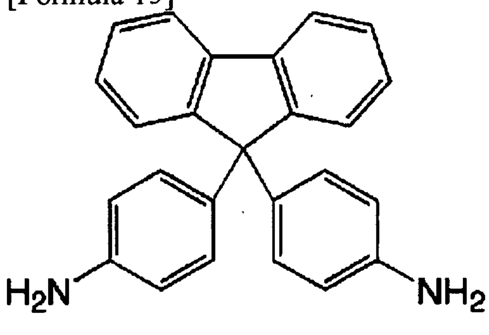
[0030]
[Formula 14]



(V I)

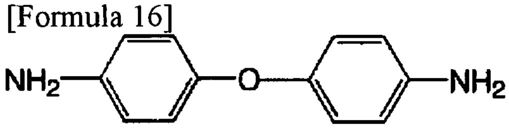
As diamine which does not contain a proton conductivity substituent For example, - diamino diphenyl ether, and 4 and 4 '4, 4'-diaminodiphenyl sulfone, A 4 and 4'-diamino diphenyl sulfide, a benzidine, a meta-phenylenediamine, A p phenylenediamine, 1,5-naphthalenediamine, 2, 6-naphthalene diamine, A bis[4-(4-amino phenoxy) phenyl] sulfone, a screw-(4-amino phenoxyphenyl) sulfide, A screw-(4-amino phenoxyphenyl) biphenyl, 1, 4-screw-(4-amino phenoxy) benzene, 1, 3-screw-(4-amino phenoxy) benzene, 3, 4'-diamino diphenyl ether, A - diamino diphenyl ether-3-sulfonamide, and 4 and 4 '3, 4'-diamino diphenyl ether-4-sulfonamide, 3 4' - - sulfonamide, and diamino diphenyl ether-3'3, 3'-diamino diphenyl ether-4-sulfonamide, A - diaminodiphenyl sulfone-3-sulfonamide, and 4 and 4 '3, 4'-diaminodiphenyl sulfone-4-sulfonamide, A - diaminodiphenyl sulfone-3'-sulfonamide, and 4 '3, 3'-diaminodiphenyl sulfone-4-sulfonamide, [3, and] A 4 and 4'-diamino diphenyl sulfide-3-sulfonamide, 3, a 4'-diamino diphenyl sulfide-4-sulfonamide, A 3 and 3'-diamino diphenyl sulfide-4-sulfonamide, 3, a 4 '- diamino diphenyl sulfide -3'-sulfonamide, A 1, 4-diaminobenzene-2-sulfonamide, 4, and 4'-diamino diphenyl ether-3-carvone amide, 3, a 4'-diamino diphenyl ether-4-carvone amide, 3, a 4 '- diamino diphenyl ether -3'-carvone amide, A - diamino diphenyl ether-4-carvone amide, and 3 and 3 '4, 4'-diamino diphenylmethane-3-carvone amide, 3, a 4'-diamino diphenylmethane-4-carvone amide, 3, a 4 '- diamino diphenylmethane -3'-carvone amide, A - diamino diphenylmethane-4-carvone amide, and 3 and 3 '4, 4'-diaminodiphenyl sulfone-3-carvone amide, 3, a 4'-diaminodiphenyl sulfone-4-carvone amide, 3, a 4 '- diaminodiphenyl sulfone -3'-carvone amide, A - diaminodiphenyl sulfone-4-carvone amide, and 3 and 3 '4, 4'-diamino diphenyl sulfide-3-carvone amide, 3, a 4'-diamino diphenyl sulfide-4-carvone amide, A 3 and 3'-diamino diphenyl sulfide-4-carvone amide, 3, a 4 '- diamino diphenyl sulfide -3'-sulfonamide, A 1, 4-diaminobenzene-2-carvone amide, 4, and 4'-bis(4-amino phenoxy) biphenyl, A bis{4-(3-amino phenoxy) phenyl} sulfone, 9, and 9-bis(4-aminophenyl) fluorene, Although a 2 and 2-bis[4-(4-amino phenoxy) phenyl] hexafluoropropane, 2, and 2-bis[4-(4-amino phenoxy) phenyl] propane, 2, and 2'-bis(trifluoromethyl)-benzidine etc. is mentioned, it is not limited to this. These are the range which does not spoil the property of a request of proton conductivity film, such as a physical property and chemical property, and may be used combining two or more sorts.

[0031] As diamine which does not contain the proton conductivity substituent used especially for this invention If the ease of carrying out, proton conductivity, etc. of membrane formation are taken into consideration in the ease of carrying out of composition of polyimide 9 expressed with following chemical formula (VII)- (X), a 9-bis(4-aminophenyl) fluorene (VII), It is desirable that it is at least one sort chosen from - diamino diphenyl ether (VIII), p phenylenediamine (IX), and 4 and 4 '2, 2' bis[-] [4-(4-amino phenoxy) phenyl] propane (X).
[0032]
[Formula 15]



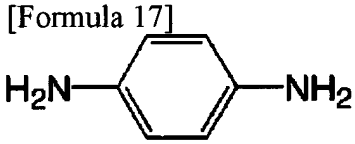
(VII)

[0033]
[Formula 16]



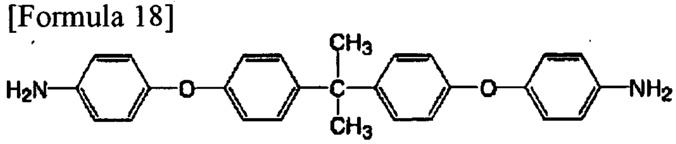
(VIII)

[0034]
[Formula 17]



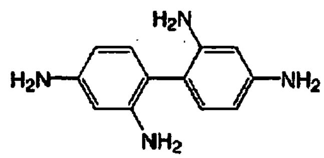
(IX)

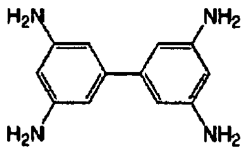
[0035]
[Formula 18]

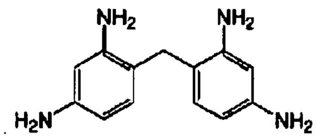


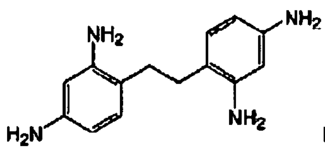
(X)

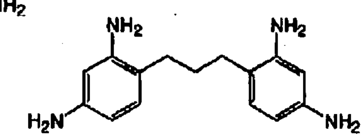
as the polyfunctional component containing three or more amino groups -- 3 and 3 - tetra-amino diphenylmethane, 1, 2 and 4, 5-tetra-aminobenzene, 3, 3', and diaminobenzidine, 3, 3', 4, and 4 '4, 4'-tetra-amino diphenyl isopropylidene, 3, 3', and '4, 4' -- although the following compound besides - TETORAAMINO diphenyl hexafluoro isopropylidene ** etc. is mentioned, it is not limited to this.
[0036]
[Formula 19]

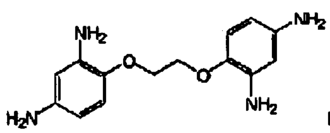


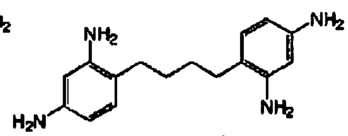


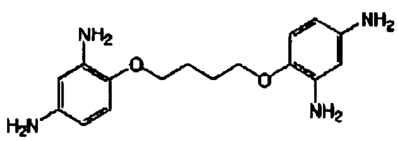




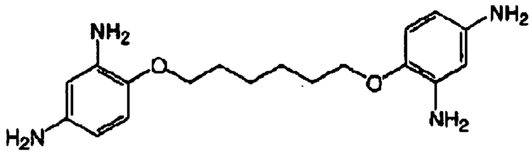


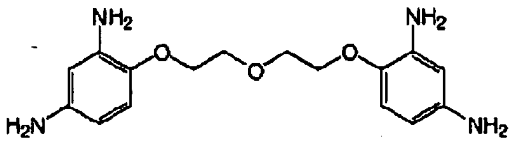


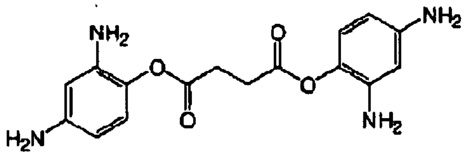


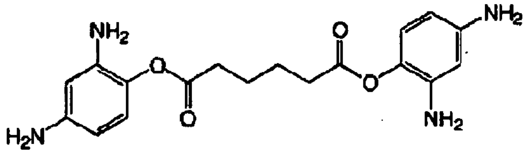


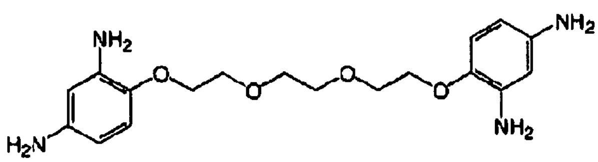
[0037]
[Formula 20]

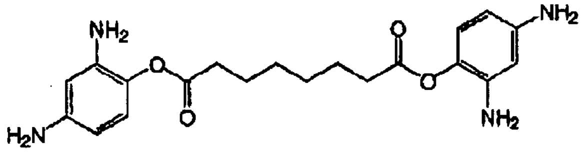




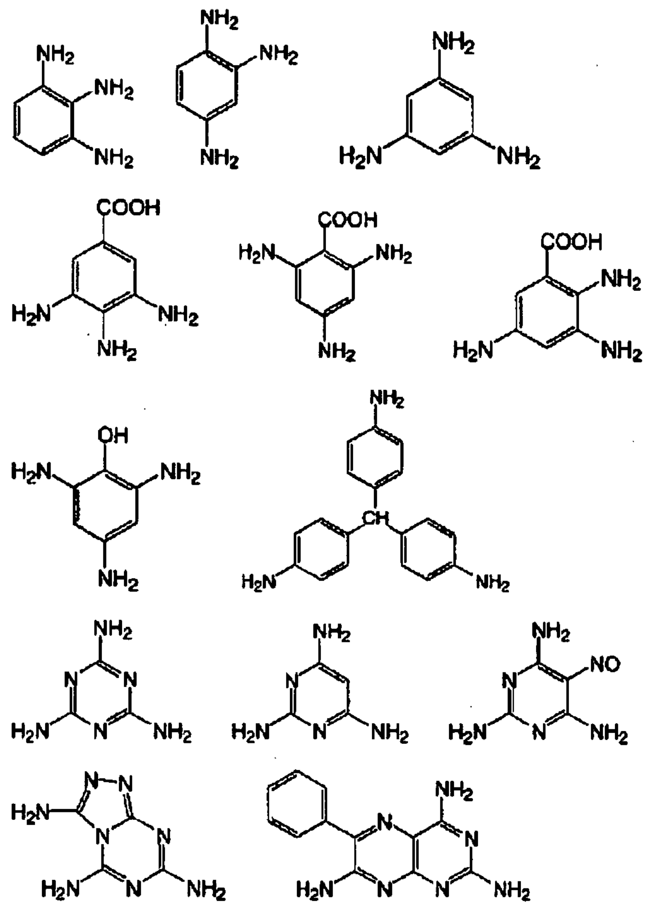




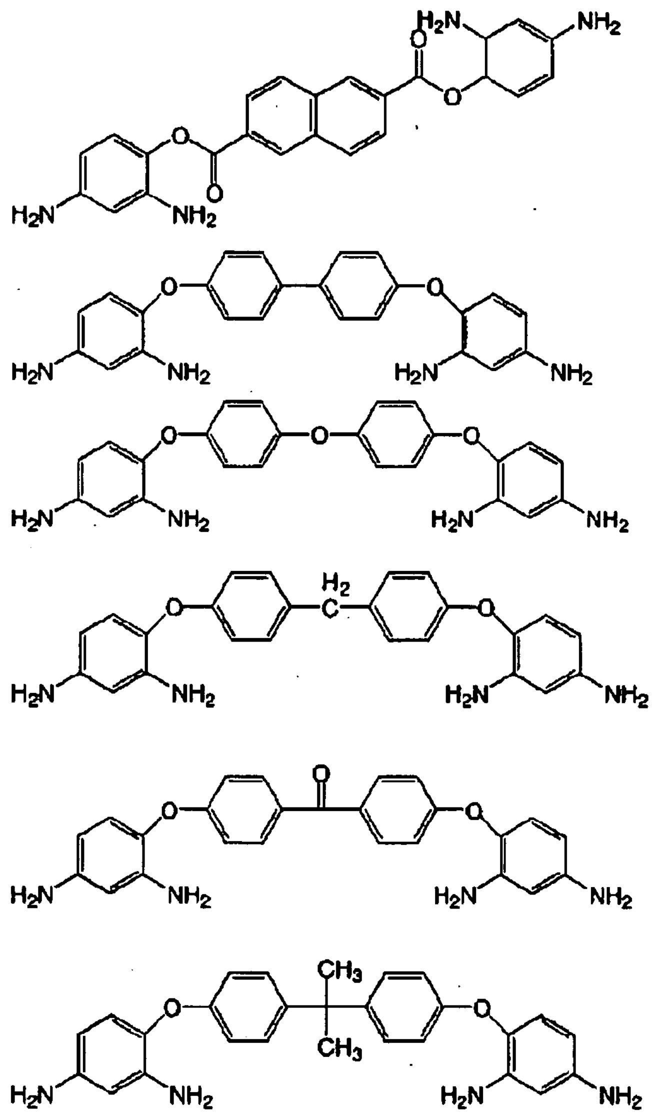




[0038]
[Formula 21]



[0039]
[Formula 22]



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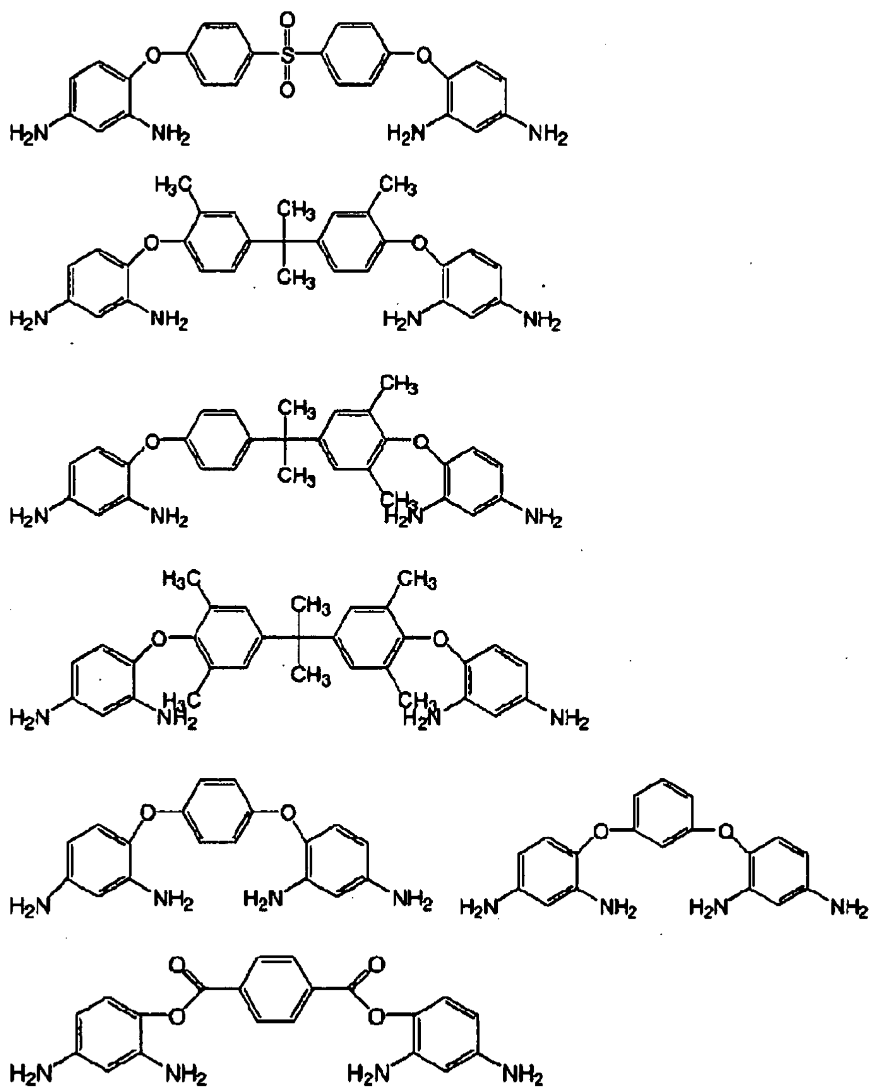
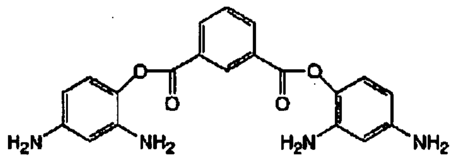
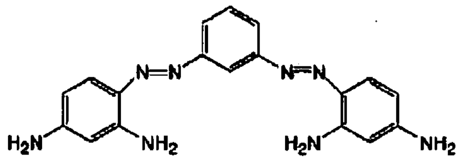
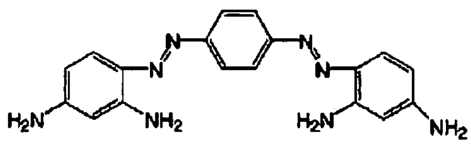
[Formula 23]

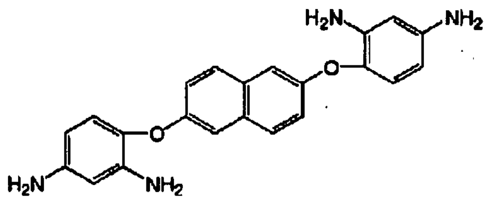


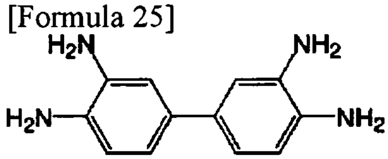
[0041]
[Formula 24]

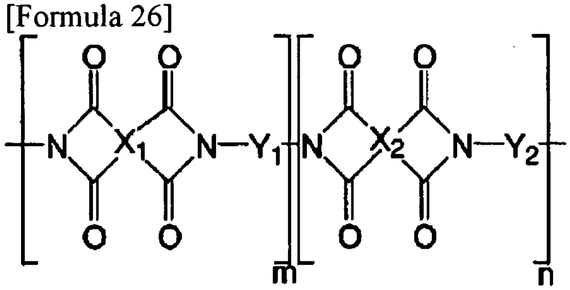








In especially this invention, when membranous physical properties etc. are taken into consideration in the ease of carrying out of film processing by the stability of a compound, the ease of industrial acquisition, and the ease of carrying out of composition of a polyimide resin constituent, it is desirable that it is the 3 and 3'-diaminobenzidine expressed with the following chemical formula (XI).
[0042]
[Formula 25]

(XI)

It is here and is the following general formula (II).
[0043]
[Formula 26]

(II)

A different tetravalent organic radical, the divalent organic radical on which Y1 contains a proton conductivity substituent, and Y2 are that X1 and X2 are the same or a thing which shows the divalent organic radical which does not contain a proton conductivity

substituent among [type. m is one or more integers and n is zero or more integers.] In the polyimide which comes out and includes the repeat unit expressed, it is desirable that the repeat unit of m is [the repeat unit of 20-85 mol % and n] a 15-80-mol % constituent ratio. Although it is based also on the monomer component to be used when the repeat unit of m is smaller than this range, the ion exchange capacity of the obtained proton conductivity film is low, and does not discover sufficient proton conduction. When larger than this range, the workability of the obtained polyimide resin constituent falls, or a possibility of becoming water solubility arises, and it becomes impossible moreover, to use it depending on an application. the monomer component (tetracarboxylic dianhydride --) which these constituent ratios use in fact The diamine containing a proton conductivity substituent, the diamine which does not contain a proton conductivity substituent, required proton conductivity, the workability (membrane formation nature) of the obtained polyimide, the mechanical strength of the acquired film, alcoholic cutoff nature, etc. are taken into consideration. Although what is necessary is just to set up suitably, the repeat unit of m is [the repeat unit of n] 30-70-mol % 30-70-mol% more preferably.

[0044] Moreover, it is desirable that the 0.1-20-mol range of repeat structural unit ** obtained according to the polyfunctional component containing three or more amino groups and the polycondensation of tetracarboxylic dianhydride is %. When smaller than this range, the branching structure and the structure of cross linkage by the polyfunctional component in a constituent decrease relatively, and that effectiveness is not enough. Moreover, when larger than this range, the workability of the proton conductivity film falls, membranous acquisition may become difficult or physical properties, such as an elastic modulus of the obtained film and reinforcement, may fall.

[0045] As for the ion exchange capacity of the proton conductivity film of this invention, it is desirable that they are 0.50 or more meq/g. When ion exchange capacity is lower than this range, sufficient proton conductivity may not be discovered as proton conductivity film.

[0046] As for the proton conductivity under the room temperature of the proton conductivity film of this invention, it is desirable that it is 1.0x10 to 2 S/more than cm. When proton conductivity is lower than this range, the direct alcoholic mold fuel cell which used this may not show sufficient generation-of-electrical-energy property.

[0047] As for the methanol transmission coefficient under the room temperature of the proton conductivity film of this invention, it is desirable that they are 1.3x10-12 (cm3 and cm) / (cm2 and s-Pa) following. When a methanol transmission coefficient is larger than this range, it becomes methanol cutoff nature equivalent to perfluoro sulfonic-acid film, such as Nafion, and there is a possibility that the fall of the cell property by the crossover of a methanol may arise.

[0048] What is necessary is just to compound composition of the polyimide which is the constituent of the proton conductivity film of this invention by one of well-known approaches. Namely, the method of heating this, performing imide-ization and obtaining a polyimide resin constituent, after isolating a polyamide acid by the approach of discharging the polyamide acid solution which compounded the polyamide acid in 1 organic solvent, and removed the solvent by technique, such as reduced pressure, or was obtained to a poor solvent etc.

2) How to isolate polyimide by the well-known approach and dry by washing if needed,

after obtaining a polyamide acid like 1, and adding the dehydrating agent further represented by the acetic anhydride, and adding a catalyst if needed and performing imide-ization chemically.
3) How to perform imide-ization thermally at the same time reduced pressure or heating removes a solvent after obtaining a polyamide acid solution like 1.
4) How to perform heating after throwing in a raw material in an organic solvent, to perform composition and the imide-ized reaction of a polyamide acid to coincidence, and to make a catalyst, an entrainer, a dehydrating agent, etc. live together if needed. **** can be illustrated.
[0049] As a solvent used for the polymerization of polyimide here For example, sulfoxide system solvents, such as dimethyl sulfoxide and diethyl sulfoxide, Formamide system solvents, such as N.N-dimethylformamide, N, and N-diethyl formamide, Acetamide system solvents, such as N,N-dimethylacetamide, N, and N-diethyl acetamide, Pyrrolidone system solvents, such as a N-methyl-2-pyrrolidone and an N-vinyl-2-pyrrolidone, A phenol, o-cresol, m-cresol, p-cresol, m-cresylic acid, Phenol system solvents, such as halogenation phenols, such as a xylenol and p-chlorophenol, and a catechol, or hexamethylphosphoramide, gamma-butyrolactone, etc. can be mentioned. Moreover, these organic solvents may be independent, or two or more sorts may use them, mixing. Furthermore, some aromatic hydrocarbon like a xylene and toluene is usable.
[0050] Moreover, when using the diamine containing proton conductivity substituents, such as a sulfonic group, as a monomer For example, aromatic series tertiary amine, such as aliphatic series tertiary amine, such as triethylamine, and dimethylaniline Heterocycle type tertiary amine, such as a pyridine, picoline, and an isoquinoline, is added to the above-mentioned organic solvent. The approach of carrying out a polymerization, after making the ammonium salt of a proton conductivity substituent form, the approach of carrying out a polymerization, after alkali metal's, such as sodium's, etc. permuting the hydrogen atom of a sulfonic group beforehand and preparing a sulfonic-acid alkali-metal salt, etc. can be illustrated. When the polymerization of the polyimide is carried out by these approaches, it is required to make a sulfuric acid, a hydrochloric acid, etc. of predetermined concentration immersed, and to make it change into the condition of proton conductivity substituents, such as a sulfonic group of a basis, the time of recovery of polyimide and after membrane formation.
[0051] The synthetic example of the polyimide resin constituent of this invention is shown below still more concretely.
They are the specified quantity and ** about at least one sort of the diamine which contains an organic solvent and a proton conductivity substituent in a synthetic example ** container.
** Add the aliphatic series tertiary amine more than the equivalent of the diamine containing a proton conductivity substituent, and stir at a room temperature 15 minutes or more preferably.
** It is specified quantity ****** about the diamine which does not contain tetracarboxylic dianhydride and a proton conductivity substituent, respectively.
** Make toluene etc. into specified quantity **** and make the temperature up of the reaction mixture to 120 degrees C or more.
** Remove carrying out azeotropy of the water to generate to toluene etc., and stir

preferably for 2 hours or more.
** Cool reaction mixture to a room temperature after carrying out ring current removal of the toluene etc.
** Drop and carry out precipitate of the reaction mixture to the mixed liquor of poor solvents, such as strong acid, methanols, etc., such as a hydrochloric acid.
** Poor solvents, such as a methanol, wash precipitate.
** Carry out reduced pressure drying at 120 degrees C, and obtain polyimide.
[0052] the above-mentioned approach -- ******** -- having had -- by one of well-known approaches, polyimide processes a film configuration and is obtained. Namely, the approach of dissolving an organic solvent in predetermined concentration, casting or applying the polyimide compounded by the approach of the I above on base materials, such as glass, considering as the shape of film, removing a solvent under predetermined conditions, and acquiring the proton conductivity film.
b) How to cast or apply the polymerization solution of the polyimide compounded by the aforementioned approach on base materials, such as glass, make it the shape of film, remove a solvent under predetermined conditions, and acquire the proton conductivity film.
c) How to dissolve an organic solvent in predetermined concentration, to cast or apply the polyamide acid which is the precursor of the polyimide compounded by the aforementioned approach on base materials, such as glass, consider as the shape of film, perform imide-izing and solvent removal under predetermined conditions, and acquire the proton conductivity film.
d) How to cast or apply the polyamide acid polymerization solution which is the precursor of the polyimide compounded by the aforementioned approach on base materials, such as glass, make it the shape of film, perform imide-izing and solvent removal under predetermined conditions, and acquire the proton conductivity film.
**** is mentioned.
[0053] The proton conductivity film acquired by the above-mentioned approach discovers the engine performance as proton conductivity film by making it change into the condition of a proton conductivity substituent by the approach mentioned above.
[0054] The organic solvent used by the above-mentioned approach has usable thing and like which are used at the time of the polymerization of this polyimide resin constituent. For example, sulfoxide system solvents, such as dimethyl sulfoxide and diethyl sulfoxide, Formamide system solvents, such as N.N-dimethylformamide, N, and N-diethyl formamide, Acetamide system solvents, such as N,N-dimethylacetamide, N, and N-diethyl acetamide, Pyrrolidone system solvents, such as a N-methyl-2-pyrrolidone and an N-vinyl-2-pyrrolidone, A phenol, o-cresol, m-cresol, p-cresol, m-cresylic acid, Phenol system solvents, such as halogenation phenols, such as a xylenol and p-chlorophenol, and a catechol, or hexamethylphosphoramide, gamma-butyrolactone, etc. can be mentioned. Moreover, these organic solvents may be independent, or two or more sorts may use them, mixing. Some aromatic hydrocarbon still like a xylene and toluene is usable. Without decomposing the structure of this polyimide or this polyamide acid besides the above, if it is made to dissolve in homogeneity, it is usable.
[0055] It is possible to enforce imide-izing and a solvent removal method by the above-mentioned approach combining the thing of arbitration. As the approach of imide-izing, both the approach by thermal processing and the approach by the chemical preparation

which uses dehydrating agents, such as an acetic anhydride, are usable. Moreover, although solvent removal should just be the conditions which can fully remove a solvent under ordinary pressure or reduced pressure, a proton conductivity substituent needs to choose desorption and the conditions which do not denaturalize.

[0056] About the thickness of the proton conductivity film of this invention, although it is selectable, when using it as proton conductivity film for direct alcoholic mold fuel cells suitably, 10-500 micrometers is desirable and 10micro - 100 micrometers are more desirable. If thickness exceeds 500 micrometers, membranous resistance may increase and the cutoff nature of alcohols, such as membranous mechanical strength and a methanol, may become inadequate in less than 10 micrometers.

[0057] Next, a drawing is quoted and explained as an example about the direct alcoholic mold fuel cell which used the proton conductivity film of this invention.

[0058] Drawing 1 is the important section sectional view of the direct alcoholic mold fuel cell which used the proton conductivity film of this invention. This consists of a configuration of passage (3) ** which sends an oxidizer into the fuel gas formed in the catalyst support gas diffusion electrode (2) in contact with the proton conductivity film (1) of this invention, and the film of (1), and the separator (4) or a liquid, and a list.

[0059] The approach of joining a catalyst support gas diffusion electrode (2) to the proton conductivity film (1) can apply the well-known approach performed by the proton conductivity film which consists for example, of perfluorocarbon-sulfonic-acid film.

[0060] Although the approach using commercial gas diffusion electrodes (product made from U.S. E-TEK etc.) can be illustrated, specifically, it is not limited to this.

[0061] As an actual approach, the field by the side of the catalyst bed of a catalyst support gas diffusion electrode (2) is doubled with both sides of the proton conductivity film (1) of this invention by using the alcoholic solution of a perfluoro sulfonic-acid giant molecule, the organic solvent solution of the polyimide of this invention, etc. as a binder, press machines, such as a hotpress machine and a roll press machine, are used, and, generally it can join at the press temperature of about 120-250 degrees C. Moreover, you may use it, preparing a catalyst support gas diffusion electrode (2) using an ingredient as shown below separately, and making it join to the proton conductivity film (1).

[0062] As an ingredient used for preparing a catalyst support gas diffusion electrode (2) here As a catalyst, as metals, such as platinum, a ruthenium, etc. which promote oxidation reaction of a fuel, and the reduction reaction of oxygen, or those alloys, and electric conduction material Although the fluorine-containing resin which has water repellence can illustrate a perfluoro sulfonic-acid system macromolecule as a base material of the above-mentioned ingredient as a binder if needed as sinking in and also cladding materials, such as a carbon cross and carbon paper, conductive matter, such as a carbon material of a particle, etc. This invention is not limited to this.

[0063] The direct alcoholic mold fuel cell of this invention according to claim 10 is obtained by inserting the proton conductivity film (1) obtained by the above approaches, and the zygote of a catalyst support gas diffusion electrode (2) among gas separators (4) with which the passage (3) which sends an oxidizer into fuel gas or a liquid, and a list was formed, such as a product made from graphite of a pair. Moreover, when a methanol is used as a fuel, a direct methanol mold fuel cell according to claim 11 is obtained. A fuel cell operates by supplying the gas (oxygen or air) which contains as a fuel the liquid or the gases which were made to evaporate of alcohols, such as a methanol, and contains

oxygen in this as an oxidizer from respectively separate passage (3) to a catalyst support gas diffusion electrode (2).
[0064] It is independent or two or more laminatings of the direct alcoholic mold fuel cell of this invention are carried out, and it can be used forming a stack and can also consider as the fuel cell system incorporating them.
[0065] As for the fuel of the direct alcoholic mold fuel cell of this invention, alcohols, such as a methanol and ethanol, are used. As a fuel directly used for a fuel cell, although formalin, a hydrazine, wood ether, etc. are examined other than said alcohols, when the safety of a fuel, the ease of industrial acquisition, the engine performance as a fuel, etc. are taken into consideration, alcohols are desirable and it is desirable to use especially a methanol and ethanol.
[0066] the approach of supplying with a liquid, after using the supply approach of alcohols as the water solution of direct or predetermined concentration, the approach of making evaporate and supplying in the state of gas, etc. -- it can illustrate -- which approach -- being usable .
[0067] The operating temperature of the direct alcoholic mold fuel cell of this invention can set up the temperature of arbitration from a room temperature to the temperature of 100 degrees C or more. Generally, a cell property shows the improving inclination as a fuel cell makes operating temperature high. However, if you are going to make it operate at the temperature of 100 degrees C or more for example, in order to control desiccation of the proton conductivity film, the pressurization of a cel will need to be the new control of the need etc. arising etc., and installation of a peripheral device. Moreover, high endurance is required also of the configuration member of the proton conductivity film or a cel to be used. On the other hand, an inclination contrary to the case of the aforementioned elevated temperature is shown as operating temperature is set as low temperature like a room temperature. Since it is one sort of a desirable gestalt to also make it operate at low temperature like a room temperature when application to noncommercial pocket devices, such as a notebook sized personal computer and a cellular phone, is assumed especially since the demand of small and simplification of the body of a fuel cell or a peripheral device is higher than a high cell property, as for the operating temperature of a direct methanol mold fuel cell, it is desirable that it is 50 degrees C or less.
[0068]
[Example] Although an example explains this invention still more concretely hereafter, in the range which is not limited at all by these examples and does not change the summary according to them, modification implementation is possible for this invention suitably. Among an example, in BDSA, 1, 4, 5, 8-naphthalene tetracarboxylic dianhydride, and FDA express a 9 and 9-bis(4-aminophenyl) fluorene, and, as for NMP, a 2 and 2'-benzidine sulfonic acid and NTDA express a N-methyl-2-pyrrolidone.
[0069] In addition, a measuring method etc. is explained in advance of an example.
[0070] (Measuring method of ion exchange capacity) It is immersed in a sodium chloride saturated water solution, and 60 degrees C of specimens are made to react all over a water bath for 3 hours. After cooling to a room temperature, ion exchange water fully washed the sample, it titrated in the 0.01-N sodium-hydroxide water solution by having used the phenolphthalein solution as the indicator, and ion exchange capacity was computed.

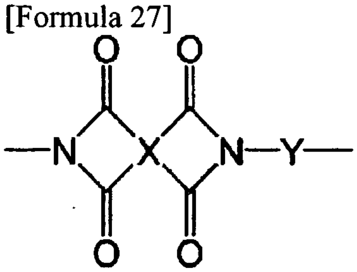
[0071] (Proton conductivity) The specimen (10mmx40mm) kept in ion exchange water is taken out, and the water on the front face of a specimen is wiped off through a filter paper. After equipping with the specimen between platinum electrodes in the inter-electrode distance of 30mm and installing in the cel made from the Teflon (trademark) of 2 pole nonclosed system, under the room temperature, on condition that electrical-potential-difference 0.2V, the membrane resistance of a specimen was measured and proton conductivity was computed by the alternating current impedance method (frequency: 42Hz - 5MHz).
[0072] (Methanol transmission coefficient) The flow Fig. of the amount measuring device of drawing 2 methanol transparency is shown. The methanol-nitrogen gas which carried out the proton conductivity film (11) at the time of **, and the measurement cel divided into two rooms, the upper part (12) and the lower part (13), was made to supply and carry out bubbling of the nitrogen gas to the methanol solution (9) heated by about 60 degrees C with a water bath (10) from a nitrogen gas cylinder (6), and was obtained is circulated in the cel upper part (12). The gas chromatograph (14) analyzed the methanol which has penetrated the inside of the proton conductivity film (11) in the cel lower part (13) purged by the gaseous helium supplied from the helium bomb (7). At this time, the temperature of a measurement cel was maintained at 25 degrees C. From the amount of methanol transparency obtained by this, the methanol transmission coefficient of the proton conductivity film (11) was computed.
[0073] (Example 1) The proton conductivity film of this invention was acquired according to the following approaches.
[0074] 0. To the separable flask of 5L, 4.30g (0.0125 mols) and a phenol were taken for BDSA, 70g and 15.18g (0.15 mols) of triethylamines were taken for 105g and p-chlorophenol, and it stirred at the room temperature under the nitrogen air current for 0.5 hours. Next, NTDA was added to 6.70g (0.025 mols), FDA was added to a 4.36g (0.0125 mols) breath, and 50g of toluene was added. It stirred at 150 degrees C under the nitrogen air current for 5 hours. The water to generate was removed at this time, carrying out azeotropy with toluene. At this time, generation water was 0.9-mL-collected and was removed. Subsequently, ring current removal of the toluene was carried out, the separable flask was ice-cooled, and reaction mixture was cooled to the room temperature. The above-mentioned reaction mixture was dropped gradually, stirring [a hydrochloric acid] the mixed solution of 1L for 26.1g and a methanol violently. Linear brown precipitate generated at this time. After washing the obtained precipitate twice by methanol 0.5L, under reduced pressure, it dried for 3 hours and 120 degrees C of polyimide were obtained.
[0075] The 20wt%NMP solution of the obtained polyimide was prepared and it applied by the thickness of 300 micrometers on the float glass, and under reduced pressure, the solvent was removed for 0.5 hours, respectively at the temperature of 50 degrees C, 100 degrees C, 150 degrees C, and 200 degrees C, and about 40-micrometer proton conductivity film was obtained. The ion exchange capacity and proton conductivity of this proton conductivity film were shown in Table 1. Moreover, the methanol transmission coefficient was shown in Table 2.
[0076] (Example 1 of a comparison) The methanol transmission coefficient of Nafion 112 (Du Pont, trademark) was measured. The result was shown in Table 2.
[0077]

[Table 1]

	イオン交換容量 (meq/g)	プロトン伝導度 (S/cm)
実施例1	1.21	1.4×10^{-2}

[0078]
[Table 2]

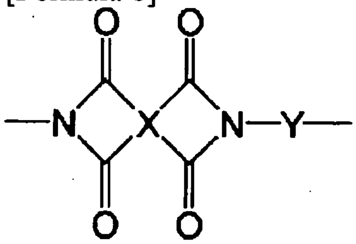
	メタノール透過係数/ $(cm^3 \cdot cm)/(cm^2 \cdot s \cdot Pa)$
実施例1	1.0×10^{-12}
比較例1	1.5×10^{-12}

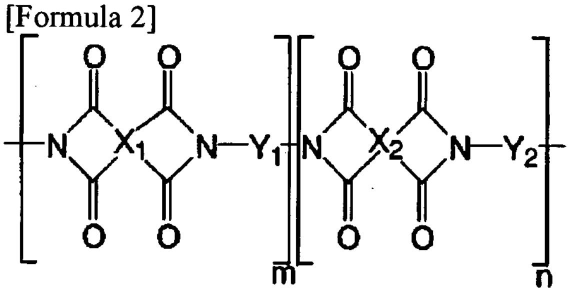
The proton conductivity film of this invention became clear [having high proton conductivity] from Table 1.
[0079] The proton conductivity film of this invention became clear [having the outstanding methanol cutoff nature] from the comparison of the example 1 of Table 2, and the example 1 of a comparison.
[0080] From the above result, the high proton conductivity which may discover engine performance with the proton conductivity film of this invention sufficient as film for direct alcoholic mold fuel cells, and the effectiveness of the outstanding methanol cutoff nature to this invention were shown.
[0081]
[Effect of the Invention] According to this invention, it is following (general formula I) [0082].
[Formula 27]

(I)

[-- X shows at least one sort of tetravalent organic radicals among a formula, Y shows at least one sort of divalent organic radicals, and a part of X and Y contain a proton conductivity substituent.] The proton conductivity film for direct alcoholic mold fuel cells which has high proton conductivity and the alcoholic outstanding cutoff nature with the proton conductivity film for direct alcoholic mold fuel cells which makes a main constituent the polyimide which comes out and includes the repeat unit expressed can be offered. Moreover, especially the direct alcoholic mold fuel cell that used it is useful as a direct methanol mold fuel cell.

CLAIMS

[Claim(s)]
[Claim 1] Proton conductivity film for direct alcoholic mold fuel cells which makes a

main constituent polyimide including the repeat unit expressed with the following general formula (I).
[Formula 1]

(I)

[-- X shows at least one sort of tetravalent organic radicals among a formula, Y shows at least one sort of divalent organic radicals, and a part of X and Y contain a proton conductivity substituent.]
[Claim 2] Proton conductivity film for direct alcoholic mold fuel cells according to claim 1 which is at least one sort chosen from the group which said proton conductivity substituent becomes from a phenolic hydroxyl group, a sulfonic group, a carboxylic-acid radical, and a phosphoric-acid radical.
[Claim 3] Proton conductivity film for direct alcoholic mold fuel cells according to claim 1 or 2 which is polyimide with which said polyimide includes the repeat unit expressed with the following general formula (II).
[Formula 2]

(I I)

A different tetravalent organic radical, the divalent organic radical on which Y1 contains a proton conductivity substituent, and Y2 are that X1 and X2 are the same or a thing which shows the divalent organic radical which does not contain a proton conductivity substituent among [type. m is one or more integers and n is zero or more integers.]
[Claim 4] Proton conductivity film for direct alcoholic mold fuel cells according to claim 3 whose repeat unit of 20-85-mol % and n the repeat unit of m of polyimide is 15-80-mol %.
[Claim 5] Proton conductivity film for direct alcoholic mold fuel cells according to claim 1 to 4 with which polyimide is characterized by including the repeat structural unit acquired according to the polyfunctional component containing three or more amino groups, and the polycondensation of tetracarboxylic dianhydride.
[Claim 6] Proton conductivity film for direct alcoholic mold fuel cells according to claim 5 the 0.1-20-mol range of whose repeat structural unit acquired according to the polyfunctional component containing three or more amino groups and the polycondensation of tetracarboxylic dianhydride is %.
[Claim 7] Proton conductivity film for direct alcoholic mold fuel cells according to claim 3 to 6 said whose polyimide is polyimide obtained according to the polycondensation of

the diamine containing tetracarboxylic dianhydride and a proton conductivity substituent, and/or the diamine which does not contain a proton conductivity substituent.

[Claim 8] Proton conductivity film for direct alcoholic mold fuel cells according to claim 7 said whose tetracarboxylic dianhydride is 1, 4, 5, and 8-naphthalene tetracarboxylic dianhydride.

[Claim 9] the diamine containing a proton conductivity substituent -- 2 and 2 - benzidine sulfonic acid, 2, 4-diaminobenzene sulfonic acid, 2, 5-diaminobenzene sulfonic acid, and '3, 3' -- the - dimethyl -4 and 4' - diamino biphenyl -6 and 6' -- the proton conductivity film for direct alcoholic mold fuel cells according to claim 7 which is at least one sort chosen from the group which consists of a - disulfon acid.

[Claim 10] Proton conductivity film for direct alcoholic mold fuel cells according to claim 7 whose diamine which does not contain a proton conductivity substituent is at least one sort chosen from the group which consists of a - diamino diphenyl ether, p phenylenediamine, and 9 and 9-bis(4-aminophenyl) fluorene, 4, and 4 '2, 2' bis[-] [4-(4-amino phenoxy) phenyl] propane.

[Claim 11] Proton conductivity film for direct alcoholic mold fuel cells according to claim 5 or 6 whose polyfunctional component containing three or more amino groups is 3 and 3'-diaminobenzidine.

[Claim 12] . Proton conductivity film for direct alcoholic mold fuel cells according to claim 1 to 11 whose ion exchange capacity of the proton conductivity film is 0.50 or more meq/g.

[Claim 13] Proton conductivity film for direct alcoholic mold fuel cells according to claim 1 to 12 whose proton conductivity under the room temperature of the proton conductivity film is 1.0x10 to 2 or more S/cm.

[Claim 14] Proton conductivity film for direct alcoholic mold fuel cells according to claim 1 to 13 whose methanol transmission coefficients of the proton conductivity film are 1.3x10-12 (cm3 and cm) / (cm2 and s-Pa) following.

[Claim 15] The direct alcoholic mold fuel cell which used the proton conductivity film according to claim 1 to 14.

[Claim 16] The direct alcoholic mold fuel cell according to claim 15 whose direct alcoholic mold fuel cell is a direct methanol mold fuel cell.

[Claim 17] The direct alcoholic mold fuel cell according to claim 15 whose direct alcoholic mold fuel cell is a direct ethanol mold fuel cell.

[Claim 18] The direct alcoholic mold fuel cell according to claim 15 whose operating temperature of a direct alcoholic mold fuel cell is 50 degrees C or less.

[Translation done.]